

## PATENT ABSTRACTS OF JAPAN

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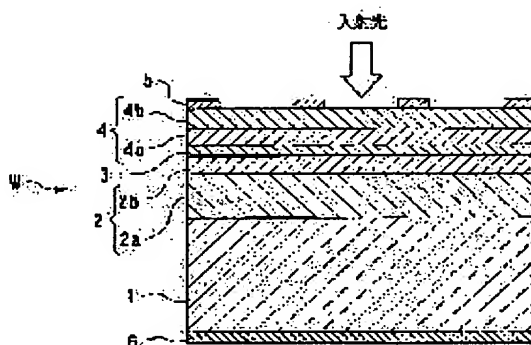
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## (54) IRON SILICIDE FILM FORMING METHOD, SEMICONDUCTOR WAFER AND OPTICAL SEMICONDUCTOR DEVICE

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide an iron silicide film forming method, a semiconductor wafer and an optical semiconductor device for forming a thick and continuous  $\beta$ -FeSi<sub>2</sub> film having a good quality.

SOLUTION: The method of forming an iron silicide film layer 4 or  $\beta$ -FeSi<sub>2</sub> on an Si wafer 1 having a crystal plane (001) on the surface comprises an SiGe layer forming step of epitaxially growing an SiGe layer 2 on the Si wafer, and an iron silicide layer forming step of epitaxially growing the iron silicide layer on the SiGe layer.



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**CLAIMS**

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[Claim(s)]

[Claim 1] The membrane formation approach of the iron silicide characterized by having the SiGe layer formation process which is the approach of forming the iron silicide layer of beta-FeSi 2 on Si wafer which has the crystal face (001) on a front face, and grows a SiGe layer epitaxially on said Si wafer, and the iron silicide layer formation process which grows said iron silicide layer epitaxially on said SiGe layer.

[Claim 2] It is the membrane formation approach of the iron silicide characterized by said SiGe layer formation process setting germanium presentation ratio in the top face of said SiGe layer to 0.35 to 0.5 in the membrane formation approach of iron silicide according to claim 1.

[Claim 3] In the membrane formation approach of iron silicide according to claim 1 or 2 said SiGe layer formation process The 1st layer formation process which grows the 1st SiGe layer epitaxially on said Si wafer, It has the 2nd layer formation process which grows the 2nd SiGe layer epitaxially on said 1st SiGe layer. Said 1st SiGe layer It is the membrane formation approach of the iron silicide which considers as the inclination presentation layer to which germanium presentation ratio was made to increase gradually, and is characterized by using said 2nd SiGe layer as the fixed presentation layer of the same germanium presentation ratio as final germanium presentation ratio of said 1st SiGe layer.

[Claim 4] It is the membrane formation approach of the iron silicide characterized by for said iron silicide layer formation process growing the distortion Si layer epitaxially on said SiGe layer in the membrane formation approach of iron silicide given in either of claims 1-3, supplying Fe to this distortion Si layer, making it react with Si of a distortion Si layer, and growing up said iron silicide layer.

[Claim 5] It is the semiconductor wafer characterized by being the semiconductor wafer with which the iron silicide layer of beta-FeSi 2 was formed on Si wafer which has the crystal face (001) on a front face, and said iron silicide layer being formed by the membrane formation approach of the iron silicide a publication by either of claims 1-4.

[Claim 6] The semiconductor wafer characterized by having the SiGe layer by which epitaxial growth was carried out on Si wafer which has the crystal face (001) on a front face, and the iron silicide layer of beta-FeSi 2 by which epitaxial growth was carried out on said SiGe layer.

[Claim 7] germanium presentation ratio [ in / on a semiconductor wafer according to claim 6 and / in said SiGe layer / the top face ] is the semiconductor wafer characterized by being 0.35 to 0.5.

[Claim 8] In a semiconductor wafer according to claim 6 or 7 said SiGe layer The 1st SiGe layer by which epitaxial growth was carried out on said Si wafer, It is formed on the 1st SiGe layer in the 2nd SiGe layer by which epitaxial growth was carried out. this -- said 1st SiGe layer It is the semiconductor wafer which is used as the inclination presentation layer to which germanium presentation ratio was made to increase gradually, and is characterized by using said 2nd SiGe layer as the fixed presentation layer of the same germanium presentation ratio as final germanium presentation ratio of said 1st SiGe layer.

[Claim 9] It is the optical semiconductor device which is an optical semiconductor device with which the barrier layer which performs light-receiving or luminescence was formed on Si wafer, and is characterized by said barrier layer being said iron silicide layer of a semiconductor wafer given in either of claims 5-8.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a semiconductor wafer and an optical semiconductor device at the membrane formation approach list of the iron silicide used for a solar-battery ingredient etc.

[0002]

[Description of the Prior Art] Unlike the iron silicide of  $\alpha$ -FeSi<sub>2</sub> which is the metal of hexagonal structure, the iron silicide of  $\beta$ -FeSi<sub>2</sub> has prismatic crystal structure, and is a direct gap semiconductor whose forbidden-band width of face is about 0.85eV. For this reason, becoming infrared light-receiving ingredients, such as an efficient solar battery, is expected because  $\beta$ -FeSi<sub>2</sub> carries out thin film formation on Si wafer since an absorption coefficient is very larger than crystalline substance silicon (it is absorption coefficient 105cm<sup>-1</sup> at the wavelength of 1.1 micrometers) and the effectiveness of photo electric conversion is high. Moreover, since As with treatment difficult in environment etc. does not need to be used for  $\beta$ -FeSi<sub>2</sub> unlike compound semiconductors, such as GaAs, it attracts attention also as a small semiconductor material of an environmental load.

[0003] Although it is necessary to make it the good continuation film in order to obtain mobility high as a light-receiving ingredient, it is difficult to form the continuation film of good  $\beta$ -FeSi<sub>2</sub> on Si wafer, and various researches are done. After forming  $\beta$ -FeSi<sub>2</sub> film on the conventional, for example, Si wafer, the technique which attaches a SiO<sub>2</sub> cap layer to the maximum front face, and prevents condensation of  $\beta$ -FeSi<sub>2</sub> is proposed (the 60th Japan Society of Applied Physics academic lecture meeting, collection of lecture drafts 4 p-ZN -2). With this technique, the  $\beta$ -FeSi<sub>2</sub> continuation film with a thickness of about 100nm is produced.

[0004]

[Problem(s) to be Solved by the Invention] The following technical problems are left behind in the above-mentioned Prior art. That is, in order to obtain light absorption effectively as a solar-battery barrier layer, the continuation film thick a figure single [ more ] is more nearly required than the thickness reported by the above-mentioned Prior art. However, when the continuation film of  $\beta$ -FeSi<sub>2</sub> was formed still more thickly, it polycrystal-ized by gap of a lattice constant with a substrate, and there was un-arranging [ that the good film was not obtained ].

[0005] This invention was made in view of the above-mentioned technical problem, and aims at providing with a semiconductor wafer and an optical semiconductor device the membrane formation approach list of the iron silicide which can form the thick continuation film in the good quality of  $\beta$ -FeSi<sub>2</sub>.

[0006]

[Means for Solving the Problem] The following configurations were used for this invention in order to solve said technical problem. That is, the membrane formation approach of the iron silicide of this invention is the approach of forming the iron silicide layer of  $\beta$ -FeSi<sub>2</sub> on Si wafer which has the crystal face (001) on a front face, and is characterized by having the SiGe layer formation process which grows a SiGe layer epitaxially on said Si wafer, and the iron silicide layer formation process which grows said iron silicide layer epitaxially on said SiGe layer. Moreover, the semiconductor wafer of this invention is characterized by having the SiGe layer by which epitaxial growth was carried out on Si wafer which has the crystal face (001) on a front face, and the iron silicide layer of  $\beta$ -FeSi<sub>2</sub> by which epitaxial growth was carried out on said SiGe layer.

[0007] In the membrane formation approach of these iron silicide, and a semiconductor wafer, since an iron silicide layer is grown epitaxially on a SiGe layer, by forming an iron silicide layer through a SiGe layer with a

larger lattice constant than Si which has the crystal face (001) on a front face, grid distortion becomes small and the continuation film of good and thick beta-FeSi<sub>2</sub> is obtained.

[0008] Moreover, as for the membrane formation approach of the iron silicide of this invention, in said SiGe layer formation process, it is desirable to set germanium presentation ratio in the top face of said SiGe layer to 0.35 to 0.5. Moreover, as for the semiconductor wafer of this invention, it is desirable that germanium presentation ratio in the top face of said SiGe layer is 0.35 to 0.5.

[0009] In the membrane formation approach of these iron silicide, and a semiconductor wafer, since germanium presentation ratio in the top face of a SiGe layer is set to 0.35 to 0.5, it becomes a SiGe layer very near the lattice constant of beta-FeSi<sub>2</sub> and grid distortion becomes very small, beta-FeSi<sub>2</sub> better film can be grown up.

[0010] Moreover, the 1st layer formation process with which, as for the membrane formation approach of the iron silicide of this invention, said SiGe layer formation process grows the 1st SiGe layer epitaxially on said Si wafer, It has the 2nd layer formation process which grows the 2nd SiGe layer epitaxially on said 1st SiGe layer. It is desirable to use said 1st SiGe layer as the inclination presentation layer to which germanium presentation ratio was made to increase gradually, and to use said 2nd SiGe layer as the fixed presentation layer of the same germanium presentation ratio as final germanium presentation ratio of said 1st SiGe layer. Moreover, the 1st SiGe layer by which, as for the semiconductor wafer of this invention, epitaxial growth of said SiGe layer was carried out on said Si wafer, It is formed on the 1st SiGe layer in the 2nd SiGe layer by which epitaxial growth was carried out. this -- It is desirable for said 1st SiGe layer to be used as the inclination presentation layer to which germanium presentation ratio was made to increase gradually, and to consider as the fixed presentation layer of the germanium presentation ratio as final germanium presentation ratio of said 1st SiGe layer with said 2nd same SiGe layer.

[0011] In the membrane formation approach of these iron silicide, and a semiconductor wafer, since an iron silicide layer is formed through the 1st SiGe layer of an inclination presentation layer, and the 2nd SiGe layer of a fixed presentation layer, the 1st SiGe layer of an inclination presentation layer can turn into a buffer layer, can control the rearrangement generated by the difference in the lattice constant on Si wafer and the top face of a SiGe layer, and can form beta-FeSi<sub>2</sub> more nearly quality film.

[0012] Moreover, the technique of the membrane formation approach of the iron silicide of this invention growing the distortion Si layer epitaxially on said SiGe layer in said iron silicide layer formation process, supplying Fe to this distortion Si layer, making it reacting with Si of a distortion Si layer, and growing up said iron silicide layer is adopted.

[0013] By the membrane formation approach of this iron silicide, since supply Fe by vacuum evaporation etc. on a SiGe layer at a distortion Si layer, it is made to react with Si of a distortion Si layer and an iron silicide layer is grown up, the membrane formation nature of the continuation film improves more.

[0014] The semiconductor wafer of this invention is a semiconductor wafer with which the iron silicide layer of beta-FeSi<sub>2</sub> was formed on Si wafer which has the crystal face (001) on a front face, and said iron silicide layer is characterized by forming membranes by the membrane formation approach of the iron silicide of above-mentioned this invention. That is, since the iron silicide layer is formed by the membrane formation approach of the iron silicide of above-mentioned this invention in this semiconductor wafer, it is especially suitable by beta-FeSi<sub>2</sub> of the good-quality continuation film as a wafer for optical semiconductor devices, such as semiconductor photo detectors, such as a solar battery, and a semi-conductor light emitting device with a luminescence wavelength of 1.5 micrometers.

[0015] The optical semiconductor device of this invention is an optical semiconductor device with which the barrier layer which performs light-receiving or luminescence was formed on Si wafer, and said barrier layer is characterized by being said iron silicide layer of the semiconductor wafer of above-mentioned this invention. since a barrier layer is said iron silicide layer of the semiconductor wafer of above-mentioned this invention in this optical semiconductor device -- the good iron silicide continuation film -- high -- optical semiconductor devices, such as a property solar battery and a light emitting device, can be obtained.

[0016]

[Embodiment of the Invention] Hereafter, 1 operation gestalt concerning this invention is explained, referring to drawing 1 and drawing 2.

[0017] Drawing 1 is what shows the cross-section structure of a solar battery (optical semiconductor device) where semiconductor wafer [ of this invention ] W and this were used. This semiconductor wafer W The SiGe

layer formation process which grows the SiGe layer (SiGe buffer layer) 2 epitaxially on the Si wafer 1 which has the crystal face (001) on a front face, It is produced by the iron silicide layer formation process which grows epitaxially the iron silicide layer (an iron silicide layer is only called hereafter) 4 of beta-FeSi 2 through the distortion Si layer 3 on the SiGe layer 2.

[0018] namely, the Si wafer 1 top which first has the crystal face (001) produced by carrying out raising growth by the CZ process as a SiGe layer formation process on a front face when the structure of the solar battery using semiconductor wafer W and this is explained together with the manufacture process -- 1st SiGe layer 2a -- growing epitaxially -- further -- this -- 2nd SiGe layer 2b is grown epitaxially on 1st SiGe layer 2a.

[0019] This 1st SiGe layer 2a considers as the inclination presentation layer to which germanium presentation ratio was made to increase gradually as shown in drawing 2, and final germanium presentation ratio is set as 0.5 (for example, 0.35) from 0.35. Moreover, let 2nd SiGe layer 2b be the fixed presentation layer of the same germanium presentation ratio 0.35-0.5 (for example, 0.35) as final germanium presentation ratio of 1st SiGe layer 2a, i.e., germanium presentation ratios. In addition, 1st SiGe layer 2a is made into the thickness of 1.5 micrometers, and let 2nd SiGe layer 2b be the thickness of 0.75 micrometers. Moreover, as for each of Si wafer 1, 1st SiGe layer 2a, and 2nd SiGe layer 2b, n mold impurity is added by high concentration.

[0020] Furthermore, the distortion Si layer 3 of n mold is grown epitaxially on 2nd SiGe layer 2b. In addition, the distortion Si layer 3 is set up more thickly than 5nm. The above-mentioned epitaxial growth is performed for example, by the reduced pressure CVD method, and SiH<sub>4</sub> grade is used for it in the distortion Si layer 3 by the SiGe layer 2, using SiH<sub>4</sub> and GeH<sub>4</sub> grade as source gas, using H<sub>2</sub> as carrier gas.

[0021] Next, the above-mentioned substrate in which the SiGe layer 2 and the distortion Si layer 3 were formed by the reduced pressure CVD method is washed SC-1, as an iron silicide layer formation process, where this substrate is heated at 650 degrees C, Fe is vapor-deposited on a substrate front face with a vacuum evaporation system, and a substrate front face is made to carry out epitaxial growth of FeSi<sub>2</sub>. In this epitaxial growth, Fe vapor-deposited by the substrate front face reacts with Si in the distortion Si layer 3 of a substrate, it is set to FeSi<sub>2</sub>, and the iron silicide layer 4 is formed. In addition, in the case of this operation gestalt, thickness is beforehand set up so that the distortion Si layer 3 may react with Fe, the iron silicide layer 4 may be formed and about 5nm in thickness may be left behind.

[0022] This iron silicide layer 4 is constituted by carrying out the laminating of n-beta-FeSi two-layer 4a of n mold, and the every 20nm p-beta-FeSi two-layer 4b of p mold to this order. In addition, as for n-beta-FeSi two-layer 4a, Co (cobalt), nickel (nickel), Pt (platinum), or Pd (palladium) is added as an n mold impurity. Moreover, even if p-beta-FeSi two-layer 4b adds Mn (manganese), Cr (chromium), V (vanadium), Ti (titanium), or aluminum (aluminum) as a p mold impurity, it is not cared about, while an iron deficit has acceptor level and undoping also serves as p mold.

[0023] The crystal face [ in / in this iron silicide layer 4 / an interface ] serves as beta-FeSi 2 (100) to Si (001), and the relation of crystal orientation is set to beta-FeSi 2 <010> or <001> to Si <110> of the Si wafer 1.

[0024] Moreover, the lattice constant of the above-mentioned Si wafer 1 is 0.543nm, and since the difference of a lattice constant with the Si wafer 1 of 2nd SiGe layer 2b of germanium presentation ratios 0.35-0.5 to which the above-mentioned iron silicide layer 4 intervenes among both although the difference of a lattice constant is 1.4 - 2.0% to the Si wafer 1 is about 1.4 - 2.0%, the grid distortion between the iron silicide layers 4 becomes small as much as possible.

[0025] With this operation gestalt, since the iron silicide layer 4 is grown epitaxially on the SiGe layer 2, by forming the iron silicide layer 4 through the SiGe layer 2 with a larger lattice constant than Si which has the crystal face (001) on a front face, grid distortion becomes small and the continuation film of good and thick beta-FeSi 2 is obtained. And since the good continuation film is obtained easily, large area-ization can be attained.

[0026] Moreover, since the iron silicide layer 4 is formed through 2nd SiGe layer 2b of 1st SiGe layer 2a of an inclination presentation layer, and a fixed presentation layer, 1st SiGe layer 2a of an inclination presentation layer can become the buffer layer which has a rearrangement control function, can control the rearrangement generated by the difference in the lattice constant of the Si wafer 1 and SiGe layer 2 top face, and can form beta-FeSi 2 more nearly quality film. Furthermore, since the distortion Si layer 3 on the SiGe layer 2 and Fe to vapor-deposit are made to react and the iron silicide layer 4 is grown up, the membrane formation nature of the continuation film improves more.

[0027] Next, while forming so that a part of p-beta-FeSi two-layer 4b may expose the Kushigata electrode 5 of aluminum thin film to the top face (on p-beta-FeSi two-layer 4b) of the above-mentioned semiconductor wafer W, a solar battery is produced by forming in the inferior surface of tongue (under the Si wafer 1) of semiconductor wafer W the rear-face electrode 6 which consists of AuSb (golden-antimony) alloy film.

[0028] since, as for the solar battery of this operation gestalt, the iron silicide layer 4 of the above-mentioned semiconductor wafer W is used for the euphotic zone (barrier layer) -- the good iron silicide continuation film -- high -- a property solar battery can be obtained.

[0029] In addition, the technical range of this invention can add various modification in the range which is not limited to the gestalt of the above-mentioned implementation and does not deviate from the meaning of this invention.

[0030] For example, although Fe vapor-deposited by forming a distortion Si layer on a SiGe layer and Si of a distortion Si layer were made to react and the iron silicide layer was formed with the above-mentioned operation gestalt, a distortion Si layer is not formed, but after performing vacuum evaporation of Si, and two or more layers vacuum evaporation of Fe by turns, annealing is performed, and you may make it form an iron silicide layer on the SiGe layer on the heated front face of a wafer.

[0031] Moreover, although the SiGe layer was made into the two-layer structure of the 1st SiGe layer of an inclination presentation layer, and the 2nd SiGe layer of a fixed presentation layer with the above-mentioned operation gestalt, it is good also as a SiGe layer of other presentation configurations. In addition, as mentioned above, while being able to reduce a rearrangement by preparing the inclination presentation layer of SiGe, grid distortion can be sharply reduced by setting final germanium presentation ratio to 0.5 from 0.35.

[0032] Moreover, with the above-mentioned operation gestalt, although applied to the solar battery as an optical semiconductor device, you may adopt it as other optical semiconductor devices. For example, you may apply to the semiconductor laser for optical communication using the iron silicide layer as a barrier layer which makes the light of a wavelength the band of 1.5 micrometers emit light etc. Furthermore, you may apply to a photosensor, the photodiode for optical communication, LED, etc. as other optical semiconductor devices. In addition, also when it is only set to  $E_g=0.83\text{eV}$  small [ of a band gap ] a little from beta-FeSi 2 of p mold of a surface layer, for example by  $x=0.08$  although it is contained also when germanium of the SiGe layer of a substrate is spread in the iron silicide layer of the above-mentioned implementation gestalt and it is doped, and set to beta-FeSi 2-xGex in this case, and germanium concentration becomes still higher, it is satisfactory as solar-battery structure.

[0033]

[Effect of the Invention] According to this invention, the following effectiveness is done so. According to the formation approach of the iron silicide layer of this invention, and the semiconductor wafer, since an iron silicide layer is grown epitaxially on a SiGe layer, by forming an iron silicide layer through a SiGe layer with a larger lattice constant than Si which has the crystal face (001) on a front face, grid distortion can become small, can obtain the continuation film of good and thick beta-FeSi 2, and can be equipped with the property which was excellent as a wafer for optical semiconductor devices, such as a solar battery.

[0034] moreover -- since a barrier layer is an iron silicide layer of the semiconductor wafer of above-mentioned this invention according to the optical semiconductor device of this invention -- the good iron silicide continuation film -- high -- optical semiconductor devices, such as a property solar battery and a light emitting device, can be obtained.

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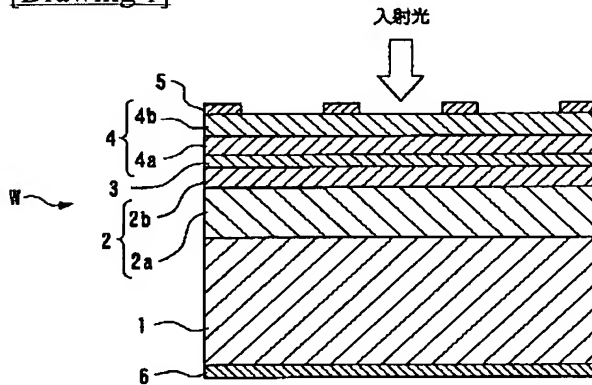
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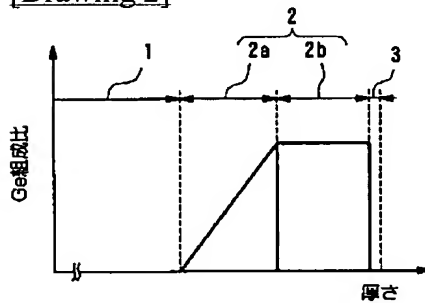
DRAWINGS

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[Drawing 1]



[Drawing 2]



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